PB81-184988

Identification and Listing of Hazardous Waste Under RCRA, Subtitle C, Section 3001 Reactivity Characteristic (40 CFR 261.23)

(U.S.) Environmental Protection Agency
Washington, DC

May 80

U.S. Department of Commerce
National Technical Information Service
NTIS

PB81-184988

BACKGROUND DOCUMENT

IDENTIFICATION AND LISTING OF HAZARDOUS WASTE UNDER RCRA, SUBTITLE C, SECTION 3001

Reactivity Characteristic (40 CFR 261.23)

This document (ms. 1941.25) provides background information and support for EPA's hazardous waste regulations

U.S. ENVIRONMENTAL PROTECTION AGENCY
May 1980

PRODUCT OF:
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3. Recipient's Accession No. PB81 184988
4. Title and Subtitle Identification and Listing of Hazardous Waste Under RCRA, Subtitle C, Section 3001 Reactivity Characteristic			5. Report Date May 1980 6.
7. Author(s)			8. Performing Organization Rept. No. 1941.25
9. Performing Organization Name and Address US Environmental Protection Agency Office of Solid Waste 401 M Street, SW Washington, DC 20460			10. Project/Task/Work Unit No. 11. Contract(C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstract (Limit: 200 words) This document is one of a series providing support for regulations issued by the U.S. Environmental Protection Agency (EPA) under Subtitle C of the Resource Conservation and Recovery Act (RCRA). The regulations represent the initial effort for nationwide control of hazardous waste from point of generation, through transportation, treatment, and storage, to point of ultimate disposal.

This document explains how EPA identified reactivety as a hazardoss waste characteristor.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms
Resource Conservation Recovery Act regulations
Hazardous waste characteristics
Reactive hazardous waste

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
	20. Security Class (This Page)	22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce

1941.25

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I. Introduction

Subtitle C of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976 creates a comprehensive "cradle-to-grave" management control system for the disposal of hazardous waste designed to protect the public health and the environment from the improper disposal of such waste. Section 3001 of that Subtitle requires EPA to identify the characteristics of and list hazardous wastes. Wastes identified or listed as hazardous will be included in the management control system created by Sections 3002-3006 and 3010. Wastes not identified or listed will be subject to the requirements for non-hazardous waste imposed by the States under Subtitle D. The Agency has determined that reactivity is a hazardous characteristic because improperly managed reactive wastes (i.e., explosives, etc.) pose a substantial present or potential danger to human health and the environment. The purpose of this document is to explain the Agency's definition of reactive wastes, to discuss the comments received on the proposed definition of reactive waste (43 FR 58956, December 18, 1978) and the changes subsequently made.

II. Proposed Regulation

Reactive waste. (1) Definition - A solid waste is a hazardous waste if a representative sample of the waste:

(i) Is normally unstable and readily undergoes violent chemical change without detonating; reacts violently with water, forms potentially explosive mixtures with water, or generates toxic gases, vapors, or fumes when mixed with water;

or is a cyanide or sulfide bearing waste which can generate toxic gases, vapors, or fumes when exposed to mild acidic or basic conditions.

(ii) Is capable of detonation or explosive reaction but requires a strong initiating source or which must be heated under confinement before initiation can take place, or which reacts explosively with water.

(iii) Is readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.

(iv) Is a forbidden explosive as defined in 49 CFR 173.51, a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.58.

NOTE--Such waste includes pyrophoric substances, explosives, autopolymerization material and oxidizing agents. If it is not apparent whether a waste is a hazardous waste using this description, then the methods cited below or equivalent methods can be used to determine if the waste is hazardous waste.

Identification method. (1) Thermally unstable waste can be identified using the Explosion Temperature Test cited in Appendix II of this Subpart (waste for which explosion, ignition, or decomposition occurs at 125°C after 5 minutes is classed as hazardous waste).

(i) Waste unstable to mechanical shock can be identified using the Bureau of Explosives impact apparatus and the tests cited in 49 CFR 173.53 (b), (c), (d), or (f), as appropriate.

III. Rationale for Proposed Regulation

A. Rationale for proposing a reactivity characteristic

Reactivity was chosen as a characteristic of hazardous waste because improperly managed reactive wastes present a danger to human health and the environment. By definition, reactive wastes are those which are capable of violently generating heat and pressure, reacting vigorously with air or water, reacting with water to generate toxic fumes, etc. The dangers which these wastes pose to transporters, waste disposal personnel, and the public are thus for the most part obvious. In the past, there have been a number of incidents of damage to persons or property which have resulted from the improper management of reactive wastes. Some of these damage incidents are listed and discussed in Appendix I.

Because of their acknowledged danger, reactive materials are often controlled by federal and state regulations and suggestions for their safe use or management are often published by public or private organizations. Some of these federal and state regulations and the guidelines for reactive materials prescribed by the National Fire Protection Association (NFPA) are listed and discussed in Appendix II.

B. Rationale for proposed reactivity definition

Reactive substances can be described as those which:

1) autopolymerize

2) are unstable with respect to heat or shock

3) are explosive

4) are strong oxidizers

5) react vigorously with air or water

6) react with water to generate toxic fumes

As can be seen from this description, the term "reactivity" encompasses a diverse and somewhat loosely conjoined class of physical properties or effects. These effects are not mutually exclusive and a particular substance might exhibit several of the properties mentioned above. For instance, certain peroxides would fall into four of the above six categories. Additionally, these categories overlap not only with each other, but also with the other characteristics. For example, the difference between flammability (conflagration) and explosiveness (deflagration) is only one of degree -- an illustration of the fact that the properties embraced by the term "reactivity" are, like the term "reactivity" itself, relative properties which have meaning only in a relative sense.

The Agency has attempted where possible to define hazardous waste characteristics in terms of specific, numerically quantified properties measurable by standardized and available testing protocols. This has proven difficult in the case of reactive wastes. The first problem with constructing a numerically quantified definition of reactive wastes arises from the fact that the term "reactivity" embraces a wide variety of different (though overlapping) effects, each of which can be triggered by an equally wide variety of initiating conditions or forces. It would be cumbersome, if not completely impractical, to construct a numerically

quantified definition which included all these different effects and their potential initiating forces. The second problem arises from the fact, as noted above, that the properties embraced by the term reactivity are relative properties. The determination that something "reacts vigorously with air or water" or is "unstable with respect to heat or shock" is a relative determination, not an absolute one. The effects being measured proceed along a continuum. Thus, it is difficult to draw the line at any particular point.

These problems are reflected in the testing methods which might be used to identify reactive substances. These methods suffer from the following generic deficiences:

1. The available tests are too specific and do not reflect the wide variety of waste management conditions.

The available tests are used to determine how a specific aspect or manifestation of waste reactivity behaves under a special and specific type of stress. For example, DTA (Differential Thermal Analysis) measures how the rate of temperature rise of the waste (one specific aspect of waste reactivity) correlates with the slow input of thermal energy (one special and specific type of stress). This would not indicate how the waste reacts to mechanical shock (a drop test would be necessary to determine that), electrical shock, whether the waste is a strong oxidizer, or even what is producing the rate of temperature change (pressure buildup, toxic or nontoxic fumes, heat of mixing, etc.). The information derived from the available tests, then, is too specialized

and does not reflect the wide variety of stresses and initiating forces likely to be found in a disposal environment.

2. Reactivity of a sample may not reflect reactivity of the whole waste:

In the case of wastes which are thermally unstable, the reactivity of the sample may not adequately reflect the reactivity of the whole waste. The kinetics of reaction are not only a function of the available initiating sources and ambient temperature, but are also a function of the mass, configuration, geometry, etc. of the sample. For a "runaway" reaction to occur, the system must transcend that steady state where the energy (heat) produced by reaction is equal to the energy transferred to the surroundings from the reacting mass. When this critical temperature is reached, the mass experiences catastrophic self-heating. This heat transfer phenomena is a function of sample size, density, and geometry. As demonstrated in equation 1:[5]

$$Cdt/dt = QVp \exp(-E/RT) + hS(T - To) \qquad (1)$$

C = mc (m=mass and c = specific heat)

T = Temperature of the material

Q = Heat of decomposition

V = Volume

p = Density

E = Activation energy

R = Gas constant

h = Heat transfer coefficient

S = Surface are of the material

As can be seen from this equation the rate of temperature rise will be affected both by the intensive properties of the waste, such as density, and the extensive properties of the waste, such as surface area and geometry. Since the extensive properties of the sample are likely to be different from the extensive properties of the whole waste, the reactivity of the sample may not reflect the reactivity of the whole waste.

3. The test results are in most cases subjective or not directly applicable.

The ideal test to use in a regulatory program is usually one which requires minimal interpretation. The majority of available reactivity testing methods are not of the "pass-fail" type. Rather, these testing methods usually produce test results which consist of a first order differential plotted against time or against a standard, from which relative reactivity can be assessed. When a test of this sort is run, it is not run to determine "reactivity" per se but rather to elicit information concerning how "fast" a material reacts (i.e. kinetic information) or how vigorously it reacts (thermodynamic information). Thus, the decision as to whether a waste is reactive requires subjective interpretation of the test results.

Additionally, the information derived from such tests may not be directly related to reactivity. For example, the test results might provide information on the activation energy - a useful, but potentially misleading bit of information since it reflects the speed of the reaction rather than the

reaction's effects. The inapplicability of some of the test results emphasizes the indefinite meaning of the term "reactivity", a term which draws its meaning from the context of its use. A chemist might think of a "reactive" substance as one with a small activation energy (the energy difference between the reactive substance's initial and transition states), i.e., one which reacts easily. The Agency, however, unlike the hypothetical chemist, is not just interested in things that react "easily" but also in things which react vigorously. It consequently needs to take into account not just the activation energy of a substance but also the heat of reaction, the molecularity of the reaction and other factors - information which the available tests often do not supply. It is, in other words, not really interested in performing a thermodynamic measurement, but rather in observing if a waste behaves in such a way as to pose a danger under normal handling conditions.

4. The standardized methods that do exist were not developed for waste testing.

Use of the available testing methods on waste materials often results in the application of standardized methods to non-standardized samples and the application of standardized methods to samples with physical consistencies the method was not designed for. If such methods are used, the results might be difficult to interpret with certainty.

The available reactivity testing methods are individually

described and evaluated in Appendix 3*. As is evident from those specific evaluations and from the preceeding discussion of the generic shortcomings of the available testing methods, none of these "type" methods are suitable for use to unequivocally determine if a waste presents a reactive hazard. For essentially the same reasons, a numerically quantified definition of reactive waste is not feasible. This is not as big a problem as might be thought on initial reflection. Most generators whose wastes are dangerous because they are reactive are well aware of this property of their waste. Reactive wastes present special problems in handling, storage and transprot. Also, reactive wastes are rarely generated from unreactive feed stocks or in processes producing unreactive products or intermediates. Furthermore, the problems posed by reactive wastes appear to be confined to a fairly narrow category of wastes. The damage incidents show that the major problems seem to be the formation of hydrogen sulfide (H_2S) from either soluble sulfides or biological degradation of sulfur containing wastes, the formation of hydrogen cyanide (HCN) from soluble cyanides, and the explosion of some

*These evaluations are taken from "A Second Appraisal of Methods for Estimating Self Reaction Hazards", E. D. Domalski, Report No. DOT/MTB/OHMD-76-6, "Classification of Test Methods for Oxidizing Materials", V.M. Kuchta, A. C. Furno, and A. C. Imof, Bureau of Mines, Report of Investigations 7954 and "Classification of Hazards of Materials-Water Reactive Materials, and Inorganic Peroxides", C. Mason and V. C. Cooper, NTIS No. PB 209-422. The evaluations are slightly modified so as to determine applicability of test methods to waste materials.

"unidentified" waste material. It will thus only be in a rare instance that a generator would be unsure of the reactivity class of the waste, or would be unable to assess whether the waste fits a prose definition, and would require the application of testing protocols to determine the reactivity of this waste. Since the available testing methods are not ideal for identifying those wastes categorized as hazardous due to reactivity, the approach chosen is to prescribe a prose description of reactive waste for self-determination by generators and to list wastes which meet this description and have been identified as reactive.

The prose definition chosen is a paraphrase of the top three of the reactive classes of the National Fire Protection Association (NFPA) reactivity classification system. The other two classes in the NFPA classification scheme are not included since these would include materials which are inert under normal handling conditions. This definition is used because it includes all aspects and types of reactivity which present a danger* and is already familiar to persons handling reactive materials. The Chemical Manufacturers Association[1] uses this definition to classify reactive wastes in its "Laboratory Waste Disposal Manual". Also, a paraphrase of this classification system is used by the Navy[2] in their hazardous waste disposal guide and is used in other hazardous materials handling guides[3,4] as a classification system.

*All wastes which have been identified as having caused damage are identified under this definition as are all commonly defined types of reactivity.

Furthermore, the States of California and Oklahoma use this system to define reactive wastes.

References

1. "Laboratory Waste Disposal Manual" Chemical Manufacturers Association (1975).

2. "NEPSS Hazardous Waste Disposal Guide", Naval Environmental Protection Support Service (1976).

3. "Handling Guide for Potentially Hazardous Materials", Material Safety Management Inc. (1975).

4. Material Data Safety Sheets.

5. E. J. Domalski, "A Second Appraisal of Methods for Estimating Self-Reaction Hazards", DOT/MTB/OHMO-76/6, G.P.O. (1976).

IV. Comments Received on the Proposed Characteristics and the Agency's Response to These Comments

The Agency received approximately forty comment letters addressing reactivity. These letters contained approximately sixty discrete recommendations or comments on the proposed regulation (in some letters more than one point was addressed). Several of the commenters felt that the proposed reactivity definition was adequate and provides desirable flexibility for the generator to use judgement. However, the large majority of comments expressed concern with the Agency's reactivity characteristic. These comments have been categorized by either content or the portion of the regulation addressed. A discussion of these follows:

A. A large majority of the comments dealt with the asserted lack of specificity and ambiguity of the prose definition.

- A number of commenters argued that the prose definition employed by the Agency is, as a general matter, too vague and should be replaced by a numerically quantified definition accompanied by appropriate testing protocols. This comment has been fully addressed in Part III above and need not be addressed further here.

- A number of commenters argued that the inclusion in the definition of wastes which "generate toxic gases, vapors, or fumes when mixed with water" and of "cyanide or sulfide bearing waste[s] which can generate toxic gases, vapors, or fumes when exposed to mild acidic

or basic conditions" needs to be made more specific. Several of the commenters suggested that a phrase such as "in harmful quantities" be inserted into the proposed regulations as follows: "...or generates toxic gases, vapors, or fumes in harmful quantities when mixed with water"; "or is a cyanide or sulfide bearing waste which can generate toxic gases, vapors, or fumes in harmful quantities when exposed to mild acidic or basic conditions." The comments on the cyanide and sulfide bearing wastes all pointed out that everything contains sulfides and most things contain cyanides (albeit in trace amounts) and many of these can generate minute quantities of hydrogen sulfide or hydrogen cyanide under mildly acidic or basic conditions. The Agency is sympathetic to these concerns, and, in anticipation of such problems, had attempted to make clear in the preamble and background documents that the Agency was leaving the determination of reactivity hazard up to the reasonable judgement of the generator based upon the generator's past experience with the waste. Taking this common sense approach, such material as soil or flyash with sulfides contamination (examples of sulfide and cyanide bearing wastes supplied by the commenters) would clearly not meet the reactivity definition. Despite this, the point made by the commenters is certainly valid. Therefore, so that there will be no confusion, the Agency has

changed the final regulation to make it more specific, as follows: "...or generates toxic gases, vapors or fumes: in quantities sufficient to presert a danger to public health or the environment when mixed with water; or is a cyanide or sulfide bearing waste which can generate toxic gases, vapors or fumes in quantities sufficient to present a danger to public health or the environment when exposed..." This would certainly better reflect our regulatory intent.

- A number of commenters advocated that the Agency specify what is meant by mildly acidic or basic conditions. One commenter specified a pH range (5 to 9), but offered no rationale as to why this particular range should be used. Since a substantal percentage of the commenters found the phrase "mildly acidic or basic" to be rather nebulous, the Agency has decided that a specific pH range should be specified. The pH range chosen is that which is considered non-hazardous by the corrosivity characteristic ($2 < pH < 12.5$). This range was chosen because any liquid outside the range is hazardous and requires management within the Subtitle C regulations. Only liquid wastes inside this range can be landfilled without regard to the strictures on compatibility imposed by the Subtitle C regulations and co-disposed with wastes containing soluble cyanides or sulfides. These are then the most stringent pH conditions which a waste could be subjected to outside of a Subtitle C facility. (Natural waters are unlikely to be outside this pH range).

- Several commenters suggested that the definition of cyanide bearing waste should distinguish between "free cyanide" and ferro cyanide" since the latter would not be available to generate hydrogen cyanide under mild acidic or basic conditions. The Agency beleives that such a clarification is not necessary. If the cyanide is unavailable under the specified acidic or basic conditions then toxic hydrogen cyanide fumes cannot be generated and the wastes containing these unavailable cyanides are not reactive. To specify these as exemptions would be redundant and by implication might lead generators to conclude that other unavailable sulfides or cyanides NOT specifically exempted, do meet the reactivity characteristic.

- A number of commenters advocated specifying the concentration of sulfide or cyanide needed to make cyanide or sulfide bearing wastes hazardous. As explained above, the identity of wastes which generate toxic gases under the conditions specified in the definition should be obvious to the generator and thus, this level of sophistication is unnecessary.

- One commenter suggested that the Agency specify a rate of evolution of toxic gas, but included no suggestions as to how to do so. The Agency is unsure of how a laboratory test method measuring gas evolution rate

could be developed which could then be meaningfully related to field conditions. Therefore, an evolution rate of toxic gas will not be included in the final regulations.

- One commenter argued that sulfides and cyanides should not be singled out in the regulations and further stated that all other potential toxic fume generators be included or, alternatively, that no toxic fume generators be included. The Agency disagrees. According to information which the Agency has in its possession (see Appendix I), the primary wastes implicated in the generation of toxic gas are sulfides and cyanides. Thus, the Agency would be remiss if it did not specify these types of wastes. If others are identified, they will be included also.

B. A number of commenters argued that the test protocols proposed in Section 250.13 (c)(2) of the regulations were expensive, unreliable and not specific enough. Additionally, several other commenters had problems with specific test protocols. (For instance, some commenters argued that the 125°C temperature adopted for the Explosion Temperature Test was not a reasonable temperature and that decomposition, as used in this test, needs to be defined.)

As a result of some preliminary work undertaken by the Agency on the Explosion Temperature Test* and after reviewing

*Evaluation of Solid Waste Extraction Procedures and Various Hazard Identification Tests (Final Report)", NUS Corporation, September, 1979, (see Appendix IV).

the comments received on these test protocols* (and in view of the generic problems with such tests, discussed above and in Appendix III), the Agency has decided to remove the test protocols from §261.23 of the regulations. The Agency agrees in general that they are are unsuitable in defining a "reactive" waste for RCRA regulatory purposes. The Agency has accordingly removed the designated test protocols from the regulations except to the extent that the Department of Transportation's definition of Class A explosives requires use of the shock instability test. As a result of this decision, the Agency does not believe it is necessary to discuss the individual concerns on the various test protocols.

C. A number of commenters argued that only under landfill conditions will a waste be subjected to strong initiating sources or heated under confinement. Therefore, they stated that since no landfilling of explosive waste is permitted, these conditions will never occur and Section 250.13(c)(1)(ii) is unnecessary.

This argument is completely circular. If Section 250.13 (c)(1)(ii) were removed from the regulations, explosive wastes would not be considered hazardous and could be disposed of in a sanitary landfill, thus subjecting the wastes to the very conditions which the commenters contend will cause the waste to explode. In any event, the Agency does not agree that a landfill is the only place in which strong initiating forces

*Comments were received from the public on the proposed reactivity test protocols both during the 90-day comment period on the proposed §3001 regulations (43 FR 58956) and in response to the solicitation of comments on the NUS report (Evaluation of Solid Waste Extraction Procedures and Various Hazard Identification Tests) which was noticed in the Federal Register on December 28, 1979 (44 FR 76827-76828)

or heating under pressure can occur. Pressure increase can be caused by confinement (e.g., a drum) together with temperature increase (e.g., caused by mixing) or gas generation (e.g., desolubilization of gases or decomposition into gases).

D. A number of commenters advocated exempting emergency situations (i.e., homemade bombs) from coverage of RCRA so that emergency teams can dispose of these explosive materials as expeditiously as possible without delay (i.e., without requiring a manifest, etc.).

The regulation already makes accommodation for cases of imminent hazard in §263.30. Thus, emergency handling of explosive wastes would be exempted by this section.

E. Other Comments

- A number of commenters advocated that all the characteristics be made as flexible as the reactivity characteristic.

  The Agency disagrees with these comments; the broad meaning and generic character of the reactivity "universe" requires a flexible characteristic. The Agency would have preferred to define reactivity by specific test protocols. However, this is not possible. The other characterisitics, (except ignitable solids) can be delineated or gauged by measurement of one (or a few) specific chemical/physical properties; therefore, the Agency will continue to define the ignitable, corrosive, and toxicity characteristic as proposed.

• One commenter argued that just because a waste may undergo a violent chemical change with another waste is no reason to consider a waste hazardous. To illustrate this point, the commenter pointed out that an acid and base when mixed will undergo violent chemical change, but that such mixing (neutralization) is a necessary part of many treatment systems and should not be prohibited.

The Agency believes this commenter to be under a misapprehension about the scope of the reactivity definition. The definition of reactivity refers to wastes which undergo violent change in an uncontrolled manner either by themselves, or when mixed with water. Therefore, the example of neutralization given by the commenter is inappropriate, in as much as that example involves the mixing of wastes. Furthermore, the Agency does not believe that the example given by the commenter is a fair representation of the hazards posed by wastes capable of undergoing a violent chemical change. The example given involves the <u>controlled</u> interaction between two wastes which is a treatment technique and thus does not reflect the hazards presented by <u>uncontrolled</u> violent chemical change characteristic of waste management situations.

• One commenter suggested that the definition of reactive waste be subdivided into sections which might be later

indexed into a compatibility chart.

The primary purpose of Section 3001 is to identify hazardous wastes, and not to dictate management techniques. Section 3004 will address the various management techniques including incompatible wastes (see §265.17 of the regulations). An appendix to the regulations (Appendix 5 in Part 265) is provided with just such information.

One commenter suggested that the Agency allow a generator to use any test that is believed appropriate for determining reactivity. Similarly, one commenter suggested that Appendix III to this background document be removed because it might discourage use of a suitable test.

This comment must be evaluated in light of the Agency's decision not to prescribe any tests for measuring reactivity. Ordinarily, when the Agency prescribes a specific test for measuring a characteristic, the generator is free to employ a different test if he can demonstrate, in accordance with the equivalency procedurees set forth in Subpart E, that his test is equivalent to the Agency-prescribed test. Since the Agency has elected not to prescribe any test protocols for measuring reactivity, the question of equivivalent test methods is largely mooted: test results are no longer determinative of whether a waste is reactive and there is nothing against which to measure equivalency.

This is not to say, however, that the use of tests by the generators is precluded. The generator is free to conduct any tests which aid him in assessing whether his waste fits within the prose definition of reactivity. However, the Agency is not bound in any way by these tests and will make its assessment of whether a waste is reactive by reference to the prose definition.

If a generator devises a test method which he believes adequately measures the reactivity of a waste, he should submit that test method to the Agency for evaluation.

One commenter suggested that the Agency address reactivity over time in the definition since a material may undergo physical and chemical changes as it ages and become extremely reactive, whereas it might not be reactive when first generated.

The Agency agrees with the commenter that some materials, such as certain ethers, can become more reactive with time. However, the Agency has no information (such as damage incidents) concerning any wastes which might present this type of problem. Additionally, the Agency is not aware of any testing method by which such wastes might be identified. Therefore, the final regulation will not address reactivity over time per se; as these wastes are identified by the Agency they will be listed in Subpart D of Part 261 of the regulations.

- One commenter objected to the Agency defining as reactive those wastes which are capable of detonation or explosive reaction if subjected to a strong initiating source or heated under confinement. The commenter asserted that many inert, non-reactive materials, including tap water, can be triggered to detonate or explode under confinement when subjected to strong, heat, pressure, or a combination of these and other initiating sources.

  The Agency disagrees with this commenter and takes specific issue with the assertion that many relatively inert substances could be made to explode when subjected to extreme heat and pressure. In any event, even if relatively inert substances could be made to explode when subjected to strong heat and pressure, these substances would not be considered reactive under the proposed definition. The Agency is only concerned with substances capable of exploding under reasonable confinement conditions -- i.e., those confinement conditions likely to be encountered in disposal environments.

V. Promulgated Regulations

As a result of EPA's review of the comments regarding the reactivity characteristic, EPA is promulgating a reactivity characteristic which significantly differs from the proposed regulations in two aspects: the thermal instability and shock instability test protocols cited in the proposed regulation has been removed and the section relative to generation of toxic gas, hydrogen cyanide and hydrogen sulfide has been

made more specific. The thermal instability test protocol was removed because the Agency determined that its interpretation was too subjective for use in a regulatory program*. (See Appendix IV).

§261.23 Characteristic of reactivity

(a) A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

(1) It is normally unstable and readily undergoes violent change without detonating.

(2) It reacts violently with water.

(3) It forms potentially explosive mixtures with water.

(4) When mixed with water, it generates toxic gases, vapors or fumes in a quantity sufficient to present danger to human health or the environment.

(5) It is a cyanide or sulfide bearing waste which, when exposed to conditions of pH between 2 and 12.5, can gen-e erate toxic gases, vapors or fumes in a quantity sufficient to present danger to human health or the environment.

(6) It is capable of detonation or explosive reaction if subjected to a strong initiating source or if heated under confinement.

(7) It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

*"Evaluation of Solid Waste Extraction Procedure and Various Hazard Identification Tests", (Final Report), NUS Corporation, September, 1979, (Appendix IV)

(8) It is a forbidden explosive as defined in 49 CFR 173.51 or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

(b) A solid waste that exhibits the characteristic of reactivity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number D003.

APPENDIX I

SELECTED DAMAGE INCIDENTS INVOLVING LAND DISPOSAL OF REACTIVE WASTE

1. Santa Cruz, California - A bulldozer operator was overcome by hydrogen sulfide (H_2S) fumes generated while mixing tanning wastes with other wastes. (Four deaths have occured in California between 1963-1976 from inhalation of H_2S from waste tanning sludge.

2. Baltimore County, Maryland - Six men were hospitalized due to the inhalation of hydrogen sulfide gas liberated from salts being landfilled.

3. Edison Township, New Jersey - A bulldozer operator was killed at a landfill when a barrel of unknown waste exploded.

4. Crosby, Texas - Residents in the area were subjected to sore throats, nauseau, and headaches when toxic fumes were released from the reaction between oily wastes and acids, dumped in an abandoned sand pit (twenty-six wells were closed by this incident).

5. Edison Township, New Jersey - Cases of conjunctivetis, eye irritation, burn on cornea, and chemical burns resulted from reactive wastes being landfilled.

6. Northern California - A drum of toluene diisocyanate (TDI) exploded, spreading extremely toxic toluene diisocyanate throughout the area.

7. Los Angeles, California - In Los Angeles County, a tank truck emptied several thousand gallons of cyanide waste onto refuse at a sanitary landfill. Another truck subsequently deposited several thousands gallons of acid waste at the same location. Reaction between the acid and the cyanide evolved large amounts of toxic hydrogen cyanide gas. A potential disaster was averted when a local chlorine dealer was quickly called to oxidize the cyanide with chlorine solution.

8. California - Sulfide waste was added to soluble oil waste in a tanker and subsequently added to other oily wastes in a tank. Later treatment fo the oil with acid to break the emulsified oil resulted in the evolution of hydrogen sulfide. Two operators were briefly affected by the gas. There was also an explosion in the tank.

9. Dundalk, Maryland - At a sanitary landfill near Dundalk, Maryland, a 2,000-gallon liquid industrial waste load containing iron sulfide, sodium sulfide, sodium carbonate and sodium thiosulfate along with smaller quantities of organic compounds was discharged into a depression atop an earth-covered area of the fill. When it reached eight to ten feet below the point of discharge, the liquid started to bubble and fume blue smoke. The smoke cloud quickly engulfed the truck driver and disabled him. Several nearby workers rushed to his aid and were also felled. During the clean-up operation, one of the county firefighters collapsed. All six of the injured were hospitalized and treated for hydrogen sulfide poisoning.

It was not determined whether the generation of hydrogen sulfide was due to the instability of the waste or the incompatibility of the waste with some of the landfill materials. (The pH of the waste was 13 when measured before it left the plant).

10. Los Angeles, California - When the laboratory drain at a Los Angeles hospital was being cleaned by scraping, the drain pipe exploded scattering fragments of metal from the pipe. Two subsequent attempts to remove the residual piping with screwdriver and hacksaw resulted in explosions in both instances. Fortunately, no one was injured in these explosions. The cause was later attributed to shock sensitive lead azide formed in the lead pipes. A test solution, containing sodium azide as a preservative, was routinely poured into the sewer drain line after use. This chemical accumulated in the pipes and reacted with the lead in the pipe to form shock-sensitive, explosive crystals of lead azide.

11. Riverside County, California - Several drums of phosphorus oxychloride, phosphorus thiochloride and thionyl chloride (all oxidizing agents) were improperly dropped off at a dump. Later, during a flood, the drums were unearthed, ruptured, and washed downstream, releasing highly toxic hydrogen chloride gas and contaminated the water.

12. California - A disposal site in central California accepted a load of solid dichromate salts (oxidizing agents) and dumped it into a pit along with pesticide formulations and empty pesticide conainers. For several days thereafter,

small fires erupted in the pit due to the oxidation of the pesticide formulations by the dichromate. Fortunately, the site personnel were able to extinguish these fires before they burned out of control.

13. Southern California - A company using toluene diisocyanate (TDI) in the manufacture of plastic and foam rubber automobile products collected and stored its TDI wastes on-site in 55-gallon metal drums with clamp type lids. After an extended period of time during which thirty such drums had been collected, a hauler was contacted to transport the wastes to a Class I site in Southern California. The hauler stored these drums in an open area at his facility for approximately two weeks. Heavy rainfall occurred during this period. Upon arrival at the disposal site a violent explosion ruptured one of the drums. There were no injuries associated with this incident. During storage some water apparently condensed or leaked into the drums through the clamp-type lids. Transportation of the drums then provided the agitation to accelerate the reaction between water and TDI. The rapid production of CO_2 caused extreme pressure build-up on one of the drums and subsequent violent rupture.

14. Southern California - In 1972 at a disposal site in Southern California, reaction of sodium chlorate (oxidizing agent) with refuse started a fire which lasted for two hours. There were no injuries associated with the incident.

Dirt contaminated with $NaClO_4$ (oxidizing agent) was drummed and tranported as "NaCl" to the sanitary landfill. The drums were emptied onto refuse. The contents of the drums were wet but reacted with the refuse to cause a fire upon dumping out. A similar incident involving $NaClO_4$ and refuse producing a fire occured in 1973. This incident involved containerized material that reacted with refuse when a container ruptured during the covering operation.

15. Southern California - A standard procedure at a Southern California disposal site for handling cyanide-bearing liquid wastes and spent caustic solutions was to inject these loads into covered wells dug into a completed section of a sanitary landfill. Routine air sampling in the vicinity of the wells detected low levels of HCN. No cyanide was detected during addition of the spent caustic to a new well. On the basis of these discoveries, use of the wells was discontinued. The cyanide gas was apparently formed in the well as a result of lowering of the pH of the waste by carbon dioxide and organic acids produced in the decomposition of refuse.

16. A delayed reaction between phosphorus oxychloride (oxidizing agent) and water in a 55 gallon drum caused violent rupture of the durm and killed a plant operator. The steam and hydrogen chloride gas generated by the reaction caused the explosion which propelled the bottom head of the drum approximately 100 yards from the scene.

APPENDIX II

STATE, FEDERAL AND NFPA REGULATIONS AND GUIDELINES

1. Texas

The Texas Water Quality Board uses the following definition: "Industrial Hazardous Waste" means any waste or mixture of waste which ... generates sudden pressure by decomposition, heat or other means and would therefore be likely to cause substantial personnel injury..." - in combination with a listing of 40 compounds.

2. State of Washington

Defines explosive using a 5" drop test, or class A explosive (see DOT) definition.

3. Pennsylvania

Combines Flammables and Explosives and uses only the following list:

(1) Munitions
(2) Blasting Materials
(3) Pressurized Cans
(4) Paint Thinners
(5) Solvents
(6) Kerosene
(7) Oils
(8) Petrochemical Waste Sludges
(9) Petroleum Waste Sludge

4. California

Uses the following definition:

"A waste, or component of waste is considered pressure generating or reactive if it:

1) Is a Forbidden or class A, B, or C explosive as defined in Title 49 CFR, Sections 173.51, 173.88, and 173.100 respectively (see DOT).

2) Is a water reactive material.

3) Is in NFPA category 2, 3, or 4 (see NFPA)".

5. Illinois

Uses the following definitions:

"Explosives" - Any waste having concentration of 1% or more of a substance described as an explosive (high, low, or permissible) by Sax (Dangerous Properties of Hazardous Materials by N. Irving Sax, Van Nostrand Reinhold) shall be considered as explosive "per se".

"Reactives" - Any waste having a composition of 5% of more of a substance that (as described by Sax) readily reacts with air, water, or other substances to produce heat and/or toxic fumes shall be considered a reactive waste. The definition includes oxidizing agents.

6. NFPA

Category 0 - Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.

Category 1 - Materials which themselves are normally unstable and readily undergo violent chemical change but do not detonate.

Also materials which may react violently with water or which may form potentially explosive mixtures with water.

Category 3 - Materials which in themselves are capable of detonation or explosive reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water.

Category 4 - Materials which in themselves are readily capable of detonation or of explosive composition or reaction at normal temperatures and pressures.

7. DOT

The Department of Transportation lists explosive wastes (these are typically propellants, explosives, initiating compounds etc.) and also specifies testing methods for liquids and solids unstable to thermal and mechanical stresses. (See 49 CFR 173.53).

Appendix III

The testing methods examined in this section[1] are separated into tests for thermal instability, (Tests I thru X) tests for impact mechanical shock instability (Tests XI a and b) tests identifying oxidizing agents, (Tests XII thru XIV) and a test identifying water reactive materials (Test XV).

1. Most of the information contained in this Appendix was taken from "A Second Appraisal of Methods for Estimating Self Reaction Hazards" E.S. Domalski Report No. DOT/MTB/OHMO-76/6.

A. Tests Identifying Wastes Unstable to Thermal Stress

I. JANAF (Joint Army Navy Air Force) Thermal Stability Test Number Six for Liquid Propellants.

1. Purpose of Test:

To determine the maximum temperatures to which thermally unstable liquids can be subjected for short periods of time without danger of explosive decomposition.

2. Operating Principle:

Under confinement in a microbomb, a liquid sample is either heated rapidly and held at a pre-determined temperature for an arbitrary time interval, or heated at a constant rate until evidence of rapid decomposition appears. Spot immersion is also possible, where the microbomb containing the sample is immersed into the bath at some elevated temperature.

3. Test Description:

A microbomb which is drilled and tapped for a thermocouple and burst disc fitting, has an internal volume of 1.3 cm^3. A liquid sample of 0.5 ml volume is used and burst diaphrams ranging from 300 to 8400 psi failure pressure can be used. The microbomb is immersed in a bath containing a bismuth-lead alloy, which melts in the range of 65.6°C(150°F) to 121.1°C(250°F). Maintenance of the bath around 93.3°C (200°F) and of the heating rate at -6.7°C (20°F) per minute, allows detection of the rate of decomposition of -16.7°C (2°F) to -15°C (5°F) per minute. An air-vibrator is used to agitate the bath and the sample in order to establish the desired heat transfer

between bath and sample. The sample temperature and the temperature difference between the bath and sample are recorded as a functions of time. The temperature at which self-decomposition begins and the rate of decomposition can be derived.

4. Test Evaluation:

This test utilizes small samples of material in good thermal contact with thermostated suroundings. The temperature of the sample can be increased with time at such a slow rate that quasi-steady states are maintained.

Rates of decomposition can be estimated from plots of the sample temperature vs. time, and from plots of the temperature difference between the sample and bath vs. time. The slope of the temperature differential curve represents the rate of heat transfer between the sample and the bath. Factors which need to be taken into account are the rate at which the bath is being heated, heating from the self-reaction of the sample, and temperature gradients in the microbomb. From a plot of the self-heating rate of the sample vs. the reciprocal of the temperature, a linear slope proportional to the activation energy should result. The precision of activation energies derived in this manner is about $\pm$ 15 percent.

5. Applicability of Test as an Index of Waste Reactivity:

The activation energy of the reaction in question, while certainly an important parameter in assessing waste reactivity

(as discussed previously) is not the only parameter. Also important are heat of reaction, waste geometry, density, the heat transfer etc. To indicate a particular activation energy as a cut-off for waste reactivity would result in many false positives and negatives.

II. ASTM (American Society for Testing and Materials) Standard Method of Test E-476-73, Thermal Instability of Confined Condensed Phase Systems (Confinement Test)

1. Purpose of Test:

To determine the temperature at which a chemical mixture will commence reaction, liberating appreciable heat or pressure, when subject to a programmed temperature rise. This method applies to solids or liquids in a closed system in air or some other atmosphere present initially under normal laboratory conditions.

2. Operating Principle:

The sample to be tested is confined in a closed vessel equipped with a burst diaphram, pressure transducer, and thermocouple. The apparatus is equilibrated in a bath at room temperature and subsequently heated at a constant rate. The temperature difference between the bath and sample, the pressure in the closed vessel, and the bath temperature are recorded continuously during the course of the test.

3. Test Description:

This apparatus is a modification of that described under the JANAF Thermal Stability Test. The sample (300 mg.) is placed in the test cell or vessel (volume 1 cm^3) and is in intimate contact with a thermocouple. The apparatus also has a burst diaphram-vent tube system to release gases formed during decomposition if the pressure reaches too high a value, and a pressure transducer to provide measurement of the total pressure inside the vessel as heat is supplied from a bath at a constant rate. The nominal heating rate of the bath is 8°C (46.4°F) to 10°C (50°F) per minute. Silicone oil is used in the range 0°C (32°F) to 370°C (698°F) and a low-melting alloy (i.e., Wood's metal) in the range 100°C (212°F) to 500°C (932°F). Recorders are used to monitor, first, the difference between the sample temperature, (T) and bath temperature, (T_0) as a function of bath temperature, and, second, pressure, (P) as a function of bath temperature. No agitation is used so as to minimize thermal lag.

4. Test Evaluation:

The threshold temperature is the lowest temperature at the left hand base of the positive peak which appears in the plot of $(T)-(T_0)$ vs T_0. The threshold temperature is an indication of the onset of thermal instability in the sample. A potential hazard exists, therefore, when the temperature of the sample exceeds this value. The instantaneous rate of pressure versus bath temperature, the maximum pressure generated and the rate of pressure rise are useful hazard parameters related to rough approximations of reaction time, and damage potential.

Examination of the rate of temperature rise of the sample, (dT/dt) and rate of temperature rise of the bath (dT_o/dt) not only allows an evaluation of the Arrhenius constants, but also provides for arbitrary scaling of the process. A simpler, and probably preferable procedure, may be to record only T_0 corresponding to a runaway condition (e.g., a specified value dT/dt dT_o/dt, or rupture of a pressure disk (there is some arbitrariness in the definition of the runaway criterion, but this feature may not be serious)), and then repeat the experiment with a different sample diameter, d. The Frank-Kamenetskii condition then gives the value of E from

$$(d1/d2)^2 = (T_{o1}/T_{o2})^2 \exp (E/R) (1/T_{o1}-1T_{o2})1.$$

This procedure obviates the necessity of evaluating A and λ, and allows immediate scaling to any size.

5. Applicability of Test as an Index of Waste Reactivity:

This test suffers from the same drawbacks as the JANAF test, i.e., the activation energy obtained from the test is not a definitive indicator of waste reactivity.

III. SELF HEATING ADIABATIC TEST

This test is run under adiabatic conditions. Conditions of this sort do not correspond to normal waste management conditions, and thus the test results are not likely to be reflective of actual waste reactivity. Since different information cannot be obtained from this test than is already available from tests I and II, and the test conditions correspond less to waste management conditions than do tests I and II, no further evaluation of this test is presented here.

IV. THERMAL SURGE TEST

1. Purpose of Test:

To determine explosion temperature (temperatures for which there is a delay time of 250 sec before explosion).

2. Operating Principle:

The discharge of a capacitor across a thin-walled tube provides the thermal stimulus to initiate explosive decomposition. The time-temperature profile of the decomposition is obtained from oscillographic records. Although the tubes are thin-walled (0.089 mm), they have considerable strength and provide a state of heavy confinement for the explosive or unstable material.

3. Test Description:

A test sample is loaded into hypodermic needle tubing which is heated, essentially instantaneously, by a capacitor discharge. The temperature and time of the explosive event are recorded from a continuous measurement of the electrical resistance of the tubing by means of an oscilloscope. The test is particularly suited to liquid material but solids can also be accomodated by melting prior to their insertion into the hypodermic needle tubing. Materials are subject to temperatures in the range of 260°C (500°F) to 1100°C (2012°F) and delay times of 50 m sec. to 50 sec. The delay time, T is given by A exp (B/RT) where A and B are constants (somewhat related to the Arrhenius pre-exponential factor and activation energy), R is the gas constant, and T is the absolute temperature.

4. Test Evaulation:

The thermal surge test supplies data on explosion

temperatures which represent conditions of minimal heat transfer. This test measures the true induction time of an explosive rather than the time required to heat up the sample. Wenograd 15 was able to show a correspondence between the temperature of the system 250 sec prior to explosion and impact test data. The activation energy parameter obtained in thermal surge test measurements under dynamic conditions are considerably lower than those determined in other measurements under isothermal conditions. This test is probably one of the best available approximations to a point source heat initiation of an unstable material in a multicomponent system.

5. Applicability of Test as an Index of Waste Reactivity

The high temperatures the test materials are subjected to in this test do not correspond to the temperatures which wastes might be subject to during management (unless the waste is subject to a strong electric discharge). For this reason, this test is unacceptable.

V. ADIABATIC STORAGE TEST

Like test III, this test is run also under adiabatic conditions, and therefore no further evaluation is presented.

VI. ISOTHERMAL STRONG TEST

This test determines the heat generation rate as a function of time and estimates the induction period at a given temperature for a material. This test is run under isothermal conditions and takes anywhere from weeks to months to complete. For these reasons, no further evaluation is presented.

VII. EXPLOSION TEMPERATURE TEST

1. Purpose of Test

To determine the temperature at which a material explodes, ignites, or decomposes after a five second immersion in a Wood's metal bath.

2. Operating Principle

This test gives an estimate of how close the explosion temperature is to ambient condition for a material, and, hence provides a measurable indication of thermal instability.

3. Test Description:

The material to be tested (25 mg.) is placed in a copper test tube (high thermal conductivity) and immersed in a Wood's metal bath. This test is made at a series of bath temperatures, and the time lag prior to explosion at each temperature is recorded. The bath temperature is lowered until a temperature is reached at which explosion, ignition, or apparent decomposition does not occur. The bath temperature working range is from about 125°C (257°F) to 400°C (752°F). The sample is removed from the bath after 5 minutes if no explosion has occurred at 360°C (680°F).

4. Test Evaluation:

The explosion time is very nearly independent of sample size provided the sample size is in the range 10 to 40 mg. Particle size is also important in providing consistent results for a group of materials. Rapid equilibration of the sample upon contact with the high temperature bath will depend upon the heat capacity and thermal conductivity of the material,

and could be a major uncertainty in the test. Explosion temperature data is a function of time and serves as useful indicators to assist in maintaining safe thermal conditions during handling and transport.

5. Applicability of Test as an Index of Waste Reactivity:

This test would seem the most suitable for our purposes. The test results are pass-fail, either an explosion, ignition, decomposition etc. takes place or not.

Problems do arise out of distortion of thermal transport from sample size. However, this is a problem with all tests. Also the Woods Metal Bath results in Cadmium fumes being generated and should only be operated in a hood. A sand bath or nonflammable oil bath might be more suitable for our purposes.

Field testing of this method indicate that it is unsuitable for use without other modifications (see Appendix IV).

VIII. EXOTHERMIC DECOMPOSITION METER TEST

1. Purpose of Test:

To determine the self-heating of a sample at small to moderate heat generation rates as a function of temperature or time.

2. Operating Principle:

A cylindrical aluminum block contains a cavity which has a Peltier element attached at the bottom and a sample is placed on the Peltier element. Heat flow from the block to the sample is measured by means of the Peltier element which provides

an electrical signal to a recording device.

3. Test Description:

A sample vessel constructed of stainless steel (volume, 2 cm^3) is positioned over a Peltier element, and both are housed inside the cavity of a cylindrical aluminum block. This central block is surrounded by mantles containing electrical heating elements in addition to an insulating layer. The electrical input to the block and mantles is maintained in such a manner as to keep the temperature difference between the block and mantles as small as possible while the block is heated linearly at about 10°C (50°F) per hour. The heat flow from the aluminum block to the sample is measured by the Peltier element. As soon as the sample begins self-reaction the heat flux to the sample starts to decrease. From a plot of the heat generation of the sample vs. the reciprocal of the absolute temperature, the activation energy can be calculated.

4. Test Evaluation:

Changes in the heat capacity of the aluminum block over the temperature range 20°C (68°F) to 200°C (392°F) will cause the temperature increase over this range to be slightly non-linear. The Peltier element is temperature dependent, and calibration using a pure copper sample having known thermal properties is recommended.

5. Applicability of Test as an Index of Waste Reactivity

This test yields activation energy and is, as a result, subject therefore to the same drawbacks as tests I and II.

IX Homogeneous Explosion Test

1. Purpose of Test:

To determine the pressure-time profile of the thermal explosion of solid or liquid materials.

2. Operating Principle:

A sample is heated under adiabatic conditions in a closed vessel until explosion occurs. The maximum rate of pressure rise and the maximum overpressure are measured as a function of time at different heat input rates.

3. Test Description:

About 100 ml of a sample is introduced into the lower part of a stainless steel vessel. The lower section is sealed off from a larger upper section above by a membrane (breaking pressure 1 bar). The larger upper section serves as a free space for the expansion of reactant or product vapors. During the main part of the induction period, pressure equalization is accomplished by a capillary tube connecting the upper and lower sections of the vessel. The two-compartment vessel is placed inside a larger vessel of 20 liter capacity which seals the former from the external surroundings. A heating mantle around the latter vessel allows heating of the inner vessel to take place as near to adiabatic conditions as possible. Around the sample vessel there is also an auxiliary heater which heats the sample at a constant (but adiabatic) rate until explosion occurs. When explosion takes place, the membrane is ruptured and expansion into the larger volume takes place. A piezo-electric pressure transducer

records the pressure prior to, during, and after explosion.

4. Test Evaluation:

Differentiation of materials which give large rates of pressure rise and overpressures can be singled out from those which give low values. Subsequent precautions for management can be taken.

5. Applicability of Test as an Index of Waste Reactivity:

This test identifies those wastes which react under thermal stress to produce large pressure gradients. This information could be of use to identify potentially reactive wastes, hazardous due to pressure generation. This type of reactive waste would also be identified by the explosion temperature test since some part of degradation or change in the sample would be apparent for the samples failing this test.

X. Differential Thermal Analysis (DTA) Test

1. Purpose of Test:

To determine exothermic and endothermic reactions in a material as heat is applied at a particular input rate.

2. Operating Principle:

The material under test and a stable reference material are heated simultaneously at the same rate. Exothermic and endothermic traces are measured using a recorder providing a temperature-time plot of the reaction process.

3. Test Description:

The material to be tested (5 to 25 mg) and a reference material (such as alumina or glass beads) are placed into identical compartments in an aluminum block. Heat is supplied

to both compartments at the same constant rate of input. Temperatures are measured using thermo-couples in conjunction with automatic recording devices so that a plot of temperature vs. time is obtained. A shift in the base line results from a change in the heat capacity or mass of the material under test. Particular care must be given to the type of temperature sensor used and to the choice of its location in the compartment inside the aluminum block. The geometry of the sample and thermal characteristics (such as thermal conductivity) of the sample will affect the shape of the DTA curve.

4. Test Evaluation:

From the exotherms and endotherms of the DTA curve, decomposition temperatures corresponding to various rates of temperature rise can be obtained. Kinetic parameters can be calculated as a result of properly varying the heating rates and assuming a constant degree of conversion of reactant when a specific thermal event (such as the peak temperature of a given exotherm) takes place. When the temperature sensors are placed in the path of the heat flow the DTA apparatus can measure the enthalpies of processes such as heats of decomposition or transition.

5. Applicability of Test as an Index of Waste Reactivity:

This test will give information as to how a waste reacts, thermally, to thermal stress. There are several problems beyond those normally associated with test's of this kind:

(1) The stress is specialized, as is the reactivity information.

(2) The test must be interpreted, and is sometimes ambiguous (as in the case where several reactions are taking place, one of which is endothermic e.g. decomposition of NH_4NO_3).

(3) Usually very small samples are used, which makes getting a representative sample even more difficult.

On the other hand, this is a standardized procedure which is familiar to industry, widely known and often used.

B. Tests for Reactive Wastes Sensitive to Mechanical Stress

A great many sensitivity tests using mechanical stimuli have been devised, mostly by the military, hence generally intended for the rating of sensitive energetic materials (explosives and propellants). Since we are interested mostly in waste commercial materials or by-products of lower sensitivity (although handled in larger amounts), the main problem is to select a few suitable tests from the large number of existing ones.

XI. Impact Test

1. Purpose of Test:

To determine the minimum drop height of a falling weight which strikes an explosive material and produces either a mild or violent decomposition reaction. Both falling weight and explosive material have a fixed and constant mass.

2. Operating Principle:

Impact energy is supplied to an explosive by a weight of constant mass which is dropped from varying heights to establish the minimum height to provide detonation, decomposition, or

charring. The impact provides rapid compression and crushing of the sample (which may involve a frictional component of crystals rubbing against crystals) and detonation ensues.

3. Test Description:

The two most prevalent impact tests are those by Picatinny Arsenal (PA) (Test XI a) and the Bureau of Mines (BM)(Test XI b).

In the PA apparatus a sample is placed in the recess of a small steel die cup, and capped with a thin brass cover. A cylindrical steel plug is placed in the center of the cover, which contains a slotted-vent and the impact of the 2 kiram weight is transferred to the steel plug.

In the BM apparatus a 20 mg. weight is always employed while the PA sample size may be varied for each experiment. The explosive sample is held between two flat parallel plates made of hardened steel and impact is transmitted to the sample by means of the upper plate. Sample decomposition is detectable by audible, visual or other sensory means.

In an apparatus used by the Bureau of Explosives (part of the Association of American Railroads) and cited in Title 49 CFR (DOT Hazardous Materials Regulations) a falling weight is guided by a pair of rigid uprights into a hammer-anvil assembly containing a 10 mg. sample of explosive. Reproducibility can become a problem here because of a non-ideal collision between the drop weight and the impact hammer since only a fraction of the drop-weight energy is transmitted to the sample.

4. Test Evaluation:

Greater confinement of the sample will limit the translational component of the impulse to a smaller area as is the case with the PA apparatus. Factors which play an influential role in the test are: materials of construction, sample thickness, sample density, hammer geometry, mass of drop weight, impact area, surface finish, the surrounding atmosphere, temperature, and pressure. Modifications can also be made to accomodate cast and liquid samples.

5. Applicability of These Tests as Indicies of Waste Reactivity:

Impact tests suffer from the drawback that the fundamental processes leading to energy release are complicated and poorly understood. Failure of good agreement between various impact tests shows that these tests contain uncontrolled parameters. On the other hand, (1) partial correlations do exist, (2) the history of the test indicates rough agreement with field experience, (3) the stimulus is of reasonable severity, (4) the tests are widely known and realtively easy to use. These facts make them useful for a partial definition of hazards.

C. Tests Identifying Oxidizing Wastes[2]

XII. Burning Rate Test for Solid Oxidizers

1. Purpose of Test:

To determine the relative fire hazard present when inorganic oxidizers are heated in the presence of wood or cellulosic substances.

[2] Most of the information contained in this section was taken from "Classification Test Methods for Oxidizing Materials" by J. M. Kutcha, A. L. Furno, and A. C. Imhof, Bureau of Mines, Report of Investigations 7594.

2. Operating Principle:

A set sample size and ratio of dried sawdust (12-50 mesh) and oxidizer is ignited and the burning rate is determined by measuring the time for the burning to propogate at least 5 inches.

3. Test Description

For the test, sawdust is initially screened to provide particles ranging in size from 12 to 50 mesh (Tyler screen series). The sawdust is dried in an oven at 101.5°C (215°F) + -15°C (5°F) for about six hours, and then test mixtures having various concentrations of the oxidizers are prepared. To obtain a uniform mixture, the materials are agitated for 10 minutes or more in a closed container. Generally, fine oxidizers are used "as received" but coarse oxidizers can be pulverized and screened to obtain samples at least as fine as the wood sawdust. For most of the oxidizers, a particle size range of about 20 to 100 mesh appears to be adequate for determining their hazard classification by this proposed test. However, where the hazard level of such materials is uncertain because of particle size considerations, the burning rates of the mixtures should also be determined using oxidizer samples that have fractions finer than 100 mesh.

Burning rates are measured using a rectangular rack that was mounted horizontally and equipped with a 60-mesh steel screen to support the sample. The sample bed is separated from the side rack mounts to insure unrestricted burning along the sides of the

sample. To form the sample bed, the sawdust-oxidizer mixture is placed on a rack between a pair of spacer bars which fixed the bed size and which are removed before ignition. The bed can also be formed in a U-shaped wire screen channel which is transferred onto the burning rack; the wire screen channel is then removed before ignition. The sample is ignited by a propane torch or similar flame source and the burning rate determined by measurements made with two fuse wire (0.5 amp) stations and an electric timer, although slow-burning mixtures can be followed visually and timed with a stopwatch. The sample bed was normally 7 inches long and the rates are measured over a distance of 5 inches and at least 1 inch from the point of ignition.

4. Test Evaluation:

This proposed test method permits classification of solid oxidizers into two or more groups based on their relative burning rates with a cellulose-type combustible such as wood sawdust. The least hazardous class includes those oxidizers that burn at low rates (<10 in/min) when mixed with the select-grade, red oak sawdust. A second class consists of oxidizers, such as the alkali nitrates and chlorates, which burn at relatively high rates (>10 in/min) when mixed with this sawdust. A third, more hazardous class should include those oxidizers, which when unmixed or mixed with a combustible, might ignite spontaneously and burn vigorously if moisture is present or if they are heated

slightly. This class would include sodium peroxide and calcium hypochlorite (69.5 percentage Cl2) which gives very high burning rates with the sawdust. A fourth class is also required for those oxidizers, such as ammonium perchlorate, which may detonate when heated under confinement or when exposed to shock.

5. Applicability of Test as an Index of Waste Oxidizing Strength

This method is designed to provide a relative measure of the increased ignition or burning hazard that may exist when inorganic oxidizers are mixed with an organic substance such as sawdust. They are not applicable to organic peroxides or to inorganic oxidizers that may detonate when heated with or without a combustible.

In the application of this test method, it must be recognized that a reliable hazard rating may not be possible for all oxidizers using a single reference combustible. If the adjacent material is not cellulosic in nature, (and in a landfill this may or maynot be the case) it is conceivable that an oxidizer may display a greater level of hazard than observed with the select-grade, red oak sawdust used in the present study.

XIII. Ignition Hazard Test for Liquid Oxidizers:

1. Purpose of Test:

To determine the relative fire hazard by exothermic reaction of liquid inorganic oxidizers with other substances or by decomposition to products which ignite or sustain a fire.

Generally, these liquids react with many organic substances and some are capable of producing spontaneous ignition when mixed with the combustible at normal or slightly elevated temperatures; some may also ignite spontaneously when heated in the absence of a combustible material.

2. Operating Principle:

In this proposed test, the ignitability or reactivity of the oxidizer sawdust mixtures is determined in an open reaction vessel using small quantities of the reactants. Temperatures up to at least 87.8°C (190°F) are used to compare the oxidizers, depending upon their reactivity. Such temperatures are not necessarily unrealistic, considering particularly the possibility of over-heating from the reaction of liquid oxidizers with contaminants. The reaction vessel in these experiments is a 200-cm^3 Pyrex beaker that is equipped with insulated heating tapes and which rested on a flat ceramic heater; however, a stainless steel beaker can also be used. Because of possible violent reactions, the reaction vessel is placed in a larger vessel of heavy-duty steel and the experiments are to be performed in a protected area.

3. Test Description:

In a trial, a predetermined quantity of the sawdust (12 to 50 mesh) is added to the reaction vessel and brought to the desired temperature. The liquid oxidizer is then cautiously injected with a long hypodermic syringe (12 inches) from behind a protective shield, and the extent of reaction is determined from continuous temperature measurements and visual observations.

The mixture temperature is measured with a 30-gage iron-constantan thermocouple protected against corrosion by a thin-walled glass sheath and located near the center of the reacting mass. Ignitions are confirmed visually since the flame reactions does not necessarily occur in the immediate area of the thermocouple; in many ignitions, the sawdust-oxidizer mixture is scattered or the flames occurred primarily near the top or outside of the test vessel. Generally, evidence of ignition is observed for periods of at least 15 minutes. If no significant temperature increase occurred, experiments are made at higher temperatures and with various sawdust-oxidizer quantities. Preliminary trials are always made with a small quantity of oxidizer (<1 ml), particularly in the case of an oxidizer of unknown reactivity.

4. Test Evaluation:

This method is not applicable to detonable liquid oxidizers, such as concentrated hydrogen peroxide (90 percent) or perchloric acid (72 percent). A shock sensitivity or thermal stability test (Test XIV) is required for evaluating these types.

5. Applicability of Test as an Index of Waste Oxidizing Strength (see Test XII, No. 5).

XIV. Self-Heating Test for Organic Peroxides[1]

1. Purpose of Test:

To determine the minimum ambient temperatures for self-heating to explosion of thermally unstable compounds in charges of specified shape but varying size.

2. Operating Principle:

The thermal decomposition of organic peroxides is observed from studying temperature-time plots to obtain the critical temperatures for explosion, heat transfer coefficient data, and apparent activation energies.

A circulating fan located within the working space of the furnace provides temperature control to within 0.5°C.

3. Test Description:

A cylindrical tube furnace is constructed of steel housed and an aluminum open-topped cylindrical container which could hold 40 to 60 grams of organic peroxide. The furnace was heated electrically over the range of 50°C (122°F) to 350°C (662°F) and could be maintained at a fixed temperature to within 0.3°C. The progress of selfheating in the peroxide sample relative to the furnace was observed by using a differential thermocouple at the center of the sample. A second thermocouple attached to the side of the container monitored the surface temperature. Temperature-time plots were recorded for different cylindrical diameters for the samples and critical temperatures were calculated.

Explosion studies were carried out with sample amounts as large as 800 grams using a somewhat modified apparatus, and similar parameters examined.

4. Test Evaluation:

The chief disadvantage of the method is the long period over which readings must be recorded and the long time required for the furnace to stabilize following a large change in operating temperature.

5. Applicability of Test as an Index of Waste Oxidizing Strength:

This test can be used to identify detonable oxidizers, but does not give any additional information other than that provided by the explosion temperature test.

D. Tests for Identifying Water Reactivity[3]

XV. Test Method for Water Reactivity[3]

1. Purpose of Test:

To identify materials which react so violently with water and provide a danger from ignition of nearby combustables, generation of flammable gases or generation of toxic fumes.

2. Operating Principle:

Water reactivity of a substance is determined either by adding a given weight of water to a given weight of material or vice versa. In either case, the rate of temperature rise and the gross temperature rise are recorded, and the gases evolved are sampled for analysis.

3. Test Description:

The sample container is a Pyrex tube, 1-3/8 inches in diameter by 10 inches long, imbedded to a depth of 3-1/2 inches in a block of insulating foam (polyurethane or polystyrene) 3 inches square by 5 inches high. A thin piece of copper 3/8 inch square and weighing 0.5 gram (about 0.025 inch thick) is silver-soldered to the tip of a chromel-alumel thermocouple which measures the temperature rise. This

[3] Test XV is taken from "Classification of Hazards of Materials--Water-Reactive Materials and Organic Peroxides", C. Mason and J. C. Cooper, NTIS Number PB-209 422.

thermocouple is placed in the Pyrex tube in such a way that the copper square is near enough to the bottom to be covered by the sample. The output of the thermocouple is fed to a suitable recorder.

An initial estimate of the severity of the reaction is made by adding 5 grams of water slowly to 0.5 gram of material with the apparatus behind a protective shield. Since either toxic or flammable gases may be evolved, the test must be carried out in a suitable fume hood. The temperature rise is measured by adding 10 grams of water slowly (10-20 sec) from behind a protective shield to 1, 2, 5, 10, and 20 grams, successively, of the sample. Measurements are continued until the temperature reaches a peak and then begins to drop. If 1, 2, and 5 grams of the material give virtually no temperature increase in 4 minutes, 10 grams of water are added to 10 grams of sample and the temperature is monitored for 1 hour to determine whether a slow reaction occurs. If the reaction is not too violent, 10 grams of water are added to 20 grams of the material to see whether a greater rise in temperature results. The procedure may be reversed by adding the material to the water in the container. The best method to determine whether a flammable or toxic gas is evolved is by chemical analysis of the gas. If a gas is evolved, a sample from the reacting material is collected through a flexible needle inserted into the reaction container to within about an inch of the reacting mixture. The sample is then analyzed on a chromatograph for flammable and/or toxic gas.

4. Test Evaluation:

The test is reproducible to within 10 percent. The test results for known reactives like the hydules of the alkali metals are positive. There seems to be little difference in the results caused by the order of mixing.

5. Applicability of Test as an Index of Waste Reactivity:

A test such as this could be used to identify pyrophoric wastes, wastes which generate toxic gases when contacted with water etc.

The test method appears to define the activity of the various materials tested. Classification of the water reactivity hazard could be based on the temperature rise which is a measure of the heat released by reaction with water. The release of flammable and/or toxic gases would create an additional hazard which could be covered by a classification such as the following:

Reactive Wastes:

Wastes which react with water to give temperature rises of 60°C (140°F) and evolve toxic or flammable gases.

Wastes which react with water to give temperature rises greater than 60°C (140°F) or evolve toxic or flammable gases.

Simplified methods of analysis for toxic gas, (particularly HCN and H2S) must be developed before this test could be considered.

APPENDIX IV

The information contained in this Appendix was extracted from "Evaluation of Solid Waste Extraction Procedures and Various Hazard Identification Tests (Final Report)", NUS Corporation, September 1979.

1. Reactivity: Explosion Temperature Test Testing Method

The Explosion Temperature Test, which is described in Attachment A to this Appendix, was used by two independent laboratories (Safety Consulting Engineers, Inc. of Rosemont, Illinois and United States Testing Company, Inc.) to determine reactivity. The purpose of this test is to determine the temperature at which a material explodes, ignites, or decomposes in a Wood's metal bath after being immersed for five minutes. Table IV-I gives the testing results obtained from the Explosion Temperature Test.

2. Conclusions and Recommendations of the Explosion Temperature Test

The proposed Explosion Temperature Test is unacceptable on the basis of the testing results. Interpretation of the testing results is too subjective.

As a replacement for the Explosion Temperature test, it is recommended that differential temperature methods be considered. For example, differential scanning calorimeter testing (i.e., differential temperature analysis) is a quick and accurate means for objectively determining the temperature at which a material will decompose or react with other materials. This system is composed of a sensitive array of temperature sensors, an adiabatic chamber, several small heating elements, and a data processing and recording system.

To determine the amount of energy absorbed or given up by a substance, a 0.1 to 5.0 mg sample is placed into the

TABLE IV-I

EXPLOSION TEMPERATURE TEST RESULTS

Sample	Laboratory	Testing Results
Ferromanganese Dust	K	5 min. at 350°C, no reaction
	L	207°C, slight reaction
Ammonium Nitrate	K	Between 300°C and 325°C, major reaction (sample decomposed, smoke visible)
	L	210°C, major reaction

adiabatic chamber and the temperature is increased via the heating elements. The data are recorded on a strip chart.

This is a very sensitive method. It can detect changes such as loss of water of hydration, phase changes, etc. It will give indications of innocuous events as well as severe ones. Endo- or exothermic reactions are clearly indicated by changes in the recorded temperature curves.

3. Supplemental General Comments (These comments are those provided by the two laboratories participating in the testing program)

1) Wood's metal is composed of bismuth (50.09%), lead (25%), tin (12.5%), and cadmium (12.5%). The use of a molten metal bath could result in potential OSHA violations because of the toxic nature of the metal fumes.
2) The proposed method is archaic and the results are highly subjective rather than objective. The method is time consuming. A thermal analysis (i.e., differential temperature analysis) is rapidly performed and the thermal properties are easily identified. Testing results are reproducible and many commercial laboratories provide these analytical services at reasonable fees.
3) Determining if a reaction has taken place by visual observations is very subjective. One laboratory sealed the copper tubes with vise-grip pliers and immersed the tubes in the bath. A reaction was judged to have taken

place if bubbles were observed in the molten bath. The test procedure gives no standard method for sealing the tubes to prevent molten metal for contacting the sample, and determining if a reaction has taken place is the opinion of the analyst.

Attachment A

EXPLOSION TEMPERATURE TEST
(March 17, 1978 Draft)

1. Purpose of Test

   To determine the temperature at which material explodes, ignites, or decomposes after a five minute immersion in a Wood's metal bath.

2. Operating Principle

   This test gives an estimate of how close the explosion temperature is to ambient conditions for a material, and hence, provides a measurable indication of thermal instability.

3. Test Description

   The material to be tested (25 mg.) is placed in a copper test tube (high thermal conductivity) and immersed in a Wood's metal bath. This test is made at a series of bath temperatures, and the time lag prior to explosion at each temperature is recorded. The bath temperature is lowered until a temperature is reached at which explosion, ignition, or apparent decomposition does not occur. The bath temperature working range is from about 125 to 400°C. The sample is removed from the bath after 5 minutes if no explosion has occured at 360°C.

Taken from "A Second Appraisal of Methods for Estimating Self Reaction Hazards," E.S. Domalski, Report No. DOT/MTB/OHMO-76/6. Department of Transportation.